SCIENCE FOR GLASS PRODUCTION

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EFFECT OF A MIXTURE OF CULLET WITH DIFFERENT COLORS ON THE PRONENESS OF CONTAINER GLASS TO FOAM UP

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The proneness of container glass obtained from a mixture of green cullet with 10 – 50% colorless or brown cullet to foam up is evaluated. An indirect method is used: the apparent density of pelleted samples heat-treated at temperatures 800, 1000, and 1200°C is monitored. It is determined that the density reaches a maximum value at 1000°C as a result of sintering and compaction and up to 1200°C it decreases because of a decrease of the solubility of gases and foaming. The density of samples sintered at 1200°C from a mixture of oxidized (green) and reduced (brown) glass decreases, while for a mixture of oxidized (green + colorless) glasses it increases. Therefore loading brown cullet into a furnace producing green glass is impermissible because there is a high risk of the melt foaming up.

Key words: container glass, foaming up, cullet.

It is well known that the use of recycled cullet in glass production makes it possible to economize raw materials and energy resources substantially. Statistically, the cullet fraction in container production is > 60% [1]. For making container glass Russia needs about 600×10^3 tons of container culler per year [2].

Secondary cullet is always contaminated with impurities of inorganic (inclusions of a refractory, metal foil, and so on) and organic (corks, labels, remains of shipment containers, and so forth) origin. It is reported in [3] that the presence of even small crystals, ceramic, stones, particles of porcelain results in rejection of the final product. Negligible quantities of iron or other ferrous impurities change the color of the final product. For example, the presence of 0.4% green glass in a melt of colorless glass cannot be neutralized, even chemically.

When a mixture of batch and cullet is heated, organic contaminants carbonize and partially interact with CO_2 (as a result of the decomposition of the carbonate component of the batch), forming CO. In the process, the reduction of sulfates and Fe^{3+} to sulfides and Fe^{2+} respectively intensifies. Between 1000 and 1250°C the sulfides and sulfates react, forming sulfur containing gases. The retention of sulfates weakens, and finally the glass can contain sulfur only in the form of sulfides [4], which signifies degradation of the fining of the melt and a change of the color hue (and even the color itself) of the glass.

For this reason, the quality criteria for recycled cullet must take account of the listed contaminants as a source of defects in the finished product [1]. On the whole the cullet preparation process must include sorting to remove foreign inorganic an organic contaminants, separation of the glass by color and hue, washing, comminution and magnetic separation, making it possible to remove from the prepared product "grounds" of metal from the milling equipment.

European glass producers impose heightened requirements on the purity of recycled glass and the preparation of high-quality container cullet. For this reason there are a number of firms that specialize in making facilities for separating glass from ferrous metals, rocks, ceramic, and so on [3] and sorting by color.

In Russia this problem is not also given its due attention, though the negative effect of using unprepared cullet is well known.

The use of a mixture of cullet of different colors different from the color of the glass being produced in the system engenders problems due to not only the appearance of extrane-

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ous hues. The combined melting of, for example, brown and green or colorless glass often is the reason for the formation of secondary bubbles, while a substantial amount of cullet with a different color entering the furnace is fraught not only with inadmissible changes of the regulated color characteristics of the product but also with foaming up of the melt, cessation of extraction, and partial outflow of the molten glass.

The system sodium sulfate + carbon is used to fine container glass [5]. To the SO_2 release

$$Na_2SO_4 \leftrightarrow Na_2O + SO_2 + 1/2O_2 \tag{1}$$

already starting during the first melting of the batch is added, in the presence of reducing additives in the batch (for example, sulfate and carbon or sulfate and sulfide), the reaction (2) which proceeds at temperature above 860°C:

$$Na_2SO_4 + Na_2S + 2SiO_2 \rightarrow 2Na_2O \cdot SiO_2 + SO_2 + S. \tag{2}$$

The solubility of sulfur with a change of the oxidation-reduction conditions of glassmaking can be described by the following equilibria:

$$1/2S_2 + O^{2-}_{(melt)} \leftrightarrow 1/2O_2 + S^{2-}_{(melt)}\ ; \tag{3}$$

$$1/2S_2 + 1.5O_2 + O^{2-}_{(melt)} \leftrightarrow SiO^{2-}_{4(melt)}\ . \tag{4}$$

White and green container glass is obtained under oxidative conditions, which lead to elevated solubility of SO_3 in the melt, while strongly reducing conditions of making brown glass improve the solubility of S^{2-}.

The objective of the present work is to evaluate the proneness of container glass, obtained from a cullet mixture with different colors, to foam up.

Glass with three colors was studied — colorless (white), green, and brown with very close oxide composition and negligible differences with respect to density, measured by hydrostatic weighing in distilled water, specifically,

white glass — 2.47 g/cm^3;
green glass — 2.48 g/cm^3;
brown glass — 2.49 g/cm^3.

The cullet was comminuted with the fraction passing through a 0.01 mm sieve separated and mixes whose compositions are shown in Table 1 were prepared.

Pellets were pressed from the mixes and heat-treated for 30 min at 800, 1000, and 120°C. After sintering the apparent density ρ_{app} of each pellet was calculated from the expression

$$\rho_{app} = \frac{m}{0.25\pi d^4 h}\ , \tag{5}$$

where m is the pellet mass, g; d is the pellet diameter, cm; and, h is the pellet height, cm.

The computational results are presented in Figs. 1 – 3.

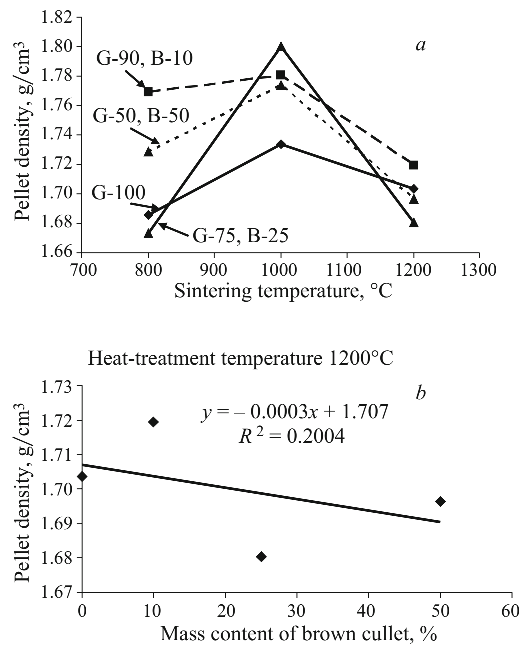

Fig. 1. Density of pellets which were obtained from green cullet with addition of brown cullet versus the temperature of the heat-treatment (*a*) and the mass content of the brown cullet in the mix (*b*).

In accordance with the assumptions used in this work, the apparent density of a pellet evidences its foaming up, i.e. intense gas release accompanied by gas filling the pores in the pellet which are closed as a result of partial melting. In this case, during glassmaking the glass will be prone to substantial foaming up, and bubbles and seeds will appear in the articles.

An apparent density increases as a result of sintering, melting, and shrinking of the sample, completely off-setting the opposite effect of a decrease of ρ_{app} as a result of gas release.

It is evident from Figs. 1*a* – 3*a* that as the sintering temperature increases the apparent density of the pellets changes nonmonotonically in practically all cases examined: as temperature increases from 800 to 1000°C it is probable that

TABLE 1. Mix Compositions

Mix	Cullet content in mixture, wt. %		
	green (G)	white (W)	brown (B)
1	100	0	0
2	90	10	0
3	75	25	0
4	50	50	0
5	90	0	10
6	75	0	25
7	50	0	50
8	0	50	50

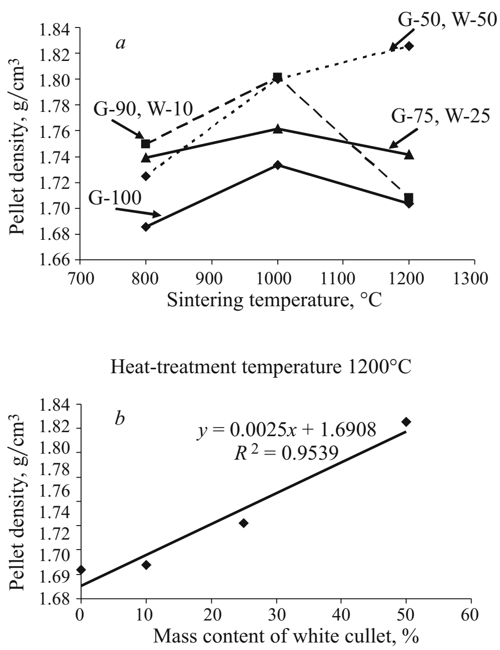

Fig. 2. Density of pellets which were obtained from green cullet with addition of white cullet versus the temperature of the heat-treatment (*a*) and the mass content of the white cullet in the mix (*b*).

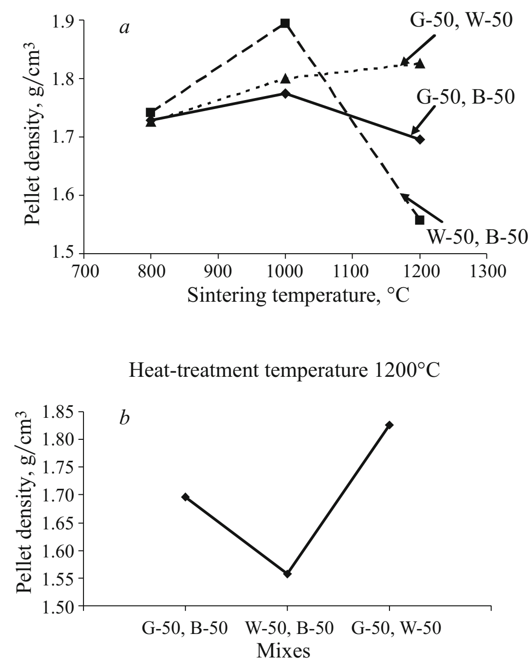

Fig. 3. Density of pellets which were obtained from identical mixtures of green, brown, and white cullet versus the temperature of the heat-treatment (*a*) and the mix composition (*b*).

only sintering and negligible melting of the samples occur, so that the value of ρ_{app} increases. At 1200°C the density decreases because, in the first place, gas release intensifies and, in the second place, melting intensifies. Pores in the pellets close and retain the gas.

As temperature increases, the solubility of the gases in the oxidized and reduced glasses decreases [5], as a result of which, naturally, they are released in the bubbles, but the dynamics of the change in the density of the pellets is related not only with this phenomenon but it also depends on the amount and nature of the gases and the viscosity of the melt formed.

Figures 1*b* and 2*b* demonstrate the change of the density of the pellets which were heat-treated at 1200°C. They were prepared from green cullet to which 10 to 50% brown (see Fig. 1*b*) or white (see Fig. 2*b*) cullet was added.

As the fraction of brown cullet increases, the apparent density of the pellets tends to decrease as a result of intense release of gas caused by contact with the oxidized (green) and reduced (brown) glass. For this reason, it should be expected that loading even a 10% brown cullet into a glass-making furnace producing green glass will cause the molten glass to foam up and massive rejection of the product. As experience shows, this is indeed observed in the real industrial technological process.

When green and white cullet are mixed together the pellet density increases. Evidently, white cullet does not have any negative effect on the quality of the green glass with respect to bubbles, but there is a risk that color characteristics of the container will change, which is undesirable and, if the color deviation is considerable, impermissible.

We also note that in the case studied here the density of samples from a mixture of green and white glass is proportional to the content of the white components in them. One probable reason for this is a difference in the viscosity of these glasses, since according to the date obtained from chemical analysis the content of viscosity-increasing SiO_2 in white glass is 0.28% lower than in green glass.

It follows from Fig. 3*b* that in order of increasing apparent density pelleted samples prepared from a two-component mixtures containing equal amounts of brown, white, and green cullet and heat-treated at 1200°C form the series

$$G + W > G + B > W + B.$$

Undoubtedly, gas release and pellet fusion occur in all cases. However, in the composition G + W made from oxidized glasses the amount of gas formed is naturally less than in samples made from oxidized + reduced glasses (G + K, W + B). The lower density of W + B pellets as compared with G + B can be explained by the minimal density and lower viscosity of white glass as compared with green glass, which makes an additive decreasing contribution to the value of ρ_{app} and favors early sintering, pore closure, and pore filling with gases which lower the apparent density of the samples.

In summary, loading even relatively small (about 10%) quantities of brown cullet into a furnace producing green glass containers is inadmissible because of the high probability of the melt foaming up and massive product rejection oc-

curring because of the presence of bubbles. White cullet does not have any negative effects on the quality of green glass with respect to bubbles.

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